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# POUR POINT REDUCTION

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This invention relates to pour depressant materials suitable for use in conjunction with hydrocarbon oils. It further relates to the means of manufacturing the aforesaid pour depressant materials. These materials are particularly adapted as additives for the reduction of the pour-point of gas oils, especially those intended for use as fuels for diesel engines, though other oils may be treated therewith.

Briefly, the invention comprises reacting urea or thiourea with hydrogenated castor oil at elevated temperatures, cooling the reaction product and adding an effective amount thereof to the hydrocarbon oil. Depending upon the amount of reaction product used, the pour-point of the treated oil may be reduced 40 or more Fahrenheit degrees below that of the original oil. The exact mechanism of the pour-point reduction is not completely known or understood at the present time.

Hydrogenated castor oil suitable for the practice of the invention consists primarily of glyceryl-12-hydroxystearate, although the commercial grades often contain minor quantities of impurities. While the invention contemplates the use of the commercial product, grades of greater purity may be satisfactory. A commercial grade of hydrogenated castor oil having the following specification is suitable in the present invention:

| | |
|---|---|
| Specific gravity, 70° F | 0.98 to 1.00 |
| Melting point (ASTM D87–22), ° F | 183 to 188 |
| Acid number | 2.0 |
| Ash, percent | Below 0.005 |
| Iodine number | 3 to 6 |
| Saponification number | 175 to 185 |

The urea (or, thiourea) suitable for reacting with hydrogenated castor oil may be that material available commercially, though containing minor quantities of impurities, or may be the pure compound.

In the operation in cold climates of diesel engines using hydrocarbon fuels having boiling ranges between approximately 350° F. and 700° F. difficulties are encountered with many otherwise satisfactory fuels due to the precipitation of wax from the oil at low temperatures. The precipitated wax at times causes plugging of the fuel lines and even prevents flow of oil from the fuel tank. Since the more paraffinic types of gas oils are preferred for diesel engine fuels because of their better combustion characteristics, as indicated by high cetane numbers, and since the more paraffinic oils have the greater tendency to precipitate wax, the situation is of major importance in the manufacture of quality diesel fuels. Similar troubles, however, are encountered in furnace oils, and the like, as well as with other oils. Accordingly, a maximum pour-point specification is commonly employed in the purchase of oils intended to be used in cold weather, the pour-point being that temperature at which the oil ceases to flow as determined by ASTM method D97–47.

To produce oils having required low pour-points from stocks of high pour-point, two general procedures are in



common use, employed either singly or in combination with each other. In one, the oil is refrigerated to a point where a sufficient amount of the wax precipitates and is removed by filtration, thereby lowering the pour-point of the filtrate oil. In the second method, certain additives are incorporated in the oil which tend to prevent precipitation of the wax. The refrigeration method requires expensive equipment and high operatnig costs to reduce the temperature of the oil sufficiently for the required amount of dewaxing. Such costs make this procedure economic only with high priced oils and, accordingly, the use of refrigeration is not commercially practical in the manufacture of diesel oils. Moreover, the pour-point depressant additives commercially available are not generally effective in lowering the pour-point of gas oils and diesel oils to the extent required.

The present invention provides a means whereby the pour-point of gas oils may be effectively reduced without resort to refrigeration. Instead, novel pour depressants, which are highly effective on waxy gas oils and diesel fuels, are made by reacting urea or thiourea with hydrogenated castor oil at about 500° F. The pour depressants of this invention are distinguishable from conventional pour depressants used in lube oils since the latter have been found ineffective in waxy gas oils. The accompanying table is illustrative of this advantageous feature.

The term "diesel fuel" as used herein denotes a fuel suitable for use in high speed diesel engines and composed primarily of gas oil. This is in contrast to heavier hydrocarbon fuels designed for use in low speed diesel engines. The term "gas oil" is used, as commonly employed by the petroleum art, to denote distillate oils having boiling ranges between about 350° F. and 750° F.

The order of addition of the reactants to form the pour-depressant materials is important. It is imperative that the urea should not be heated up to 500° F. and the hydrogenated castor oil then added because urea undergoes self-condensation when heated to form biuret or cyanic acid which polymerizes to polycyanic acid. This eliminates urea from later reaction with the hydrogenated castor oil. Alternatively, urea and hydrogenated castor oil may be heated up together to form the pour depressant reaction products, or, the hydrogenated castor oil may be heated alone to the proper reaction temperature then with the addition of urea the heating continued to maintain this temperature. To avoid any possibility of urea self-condensations, it is suggested that first the hydrogenated castor oil be heated and then the urea added in an appropriate amount.

While the reaction between hydrogenated castor oil and urea is presumed to occur between the $NH_2$ groups of urea and the alcoholic OH groups of the hydrogenated castor oil requiring a mole ratio of 3 moles of urea to 2 moles of hydrogenated castor oil, effective pour depressants can be produced by varying the amounts of reactants over fairly wide limits. For example, reactions involving 0.3 mole of urea and 2 moles of hydrogenated castor oil will yield satisfactory products as is also found with reactions with 15 moles of urea and 2 moles of hydrogenated castor oil.

Similarly, the temperature of reaction may vary over the range of 350° F. to 600° F. Effective pour depressants can be made by heating the reaction mass for about one hour at 350° F., then increasing the temperature to 600° F. and finally allowing the reactants to cool. While the preferred time and temperature for the reaction is one hour at 500° F., it is possible to produce an acceptable material after heating for one-half hour at 350° F. Moreover, a suitable product can be made by heating the reactants to 600° F. for one-half hour. However, above 600° F. the reaction mixture is prone to catch

on fire as well as to form carbon deposits on the sides of the reaction vessel. Furthermore, prolonged heating, e.g. 8 hours at 500° F., decreases the effectiveness of the pour depressant qualities of the additive although this treatment does not destroy these qualities completely.

When the reactants are heated together beyond 300° F. the reaction results in the evolution of gases. At 500° F. the evolution of gases is vigorous and subsides after about 15 minutes of continued heating. The resulting reaction mass comprises two phases. The lower phase is a white lumpy solid and the upper phase is a mobile liquid which upon cooling becomes a soft wax-like material. The upper phase constitutes the pour depressant of the present invention, and, it may be separated from the lower phase by filtration while maintaining a suitably high temperature, or, by decantation.

The following examples are offered for the purpose of illustrating applications of the present invention in specific instances:

## EXAMPLE I

1000 parts by weight of hydrogenated castor oil are heated to 500° F. To this are added slowly 101 parts by weight of urea while maintaining the temperature above 450° F. The mixture is heated for 1 hour at 500° F. whereby two layers form. The upper layer constituting the pour depressant product is separated from the lower layer by decantation and then cooled. Upon dissolving a 1% by weight concentration of the decanted product in +50° F. pour point gas oil it is founded that the pour point is reduced to —15° F.

## EXAMPLE II

1000 parts by weight of hydrogenated castor oil are treated as in Example I except that 10.1 parts by weight of urea are used. A 1% by weight concentration of the decanted product in +40° F. pour point gas oil reduces the pour point to —20° F.

## EXAMPLE III

1000 parts by weight of hydrogenated castor oil are treated as in Example I except that 500 parts by weight of urea are used. A 1% by weight concentration of the decanted product in +40° F. pour point gas oil reduces the pour point to —20° F.

## EXAMPLE IV

1000 parts by weight of hydrogenated castor oil and 101 parts by weight of urea are heated to 350° F. and the temperature maintained for 30 minutes whereby the pour point depressant reaction product forms as the upper layer. This upper layer is decanted and cooled. A 1% by weight concentration of the decanted product is dissolved in +50° F. pour point gas oil. The pour point of the gas oil is thereby reduced to +40° F.

## EXAMPLE V

1000 parts by weight of hydrogenated castor oil and 128 parts by weight of thiourea are heated together at 500° F. for 1 hour whereby the pour depressant material forms as an upper layer which is decanted from the lower layer. The decanted product is then cooled and a 1% by weight concentration thereof is dissolved in +50° F. pour point gas oil. The pour point of the gas oil is found to be —15° F.

While the foregoing examples indicate that wide ranges in reaction times and temperatures as well as varying proportions of reactants result in high quality pour depressant materials, the accompanying table shows the applicability of the products of the invention in reducing the pour-point of gas oils derived from various crudes. In each case illustrating the present invention the mole ratio of urea to hydrogenated castor oil is 3:2 while the time and temperature of reaction is 1 hour at 500° F., the urea being added after reaction temperature is reached.

It will be apparent from an examination of the table that the product of the invention is a very effective pour point depressant and that the invention solves a problem not readily solved by other commercially available materials such as, for example, poly methacrylates. Tests indicate that the pour depressants described herein are of general application to most gas oils.

While a 1% by weight concentration of reaction product is recommended for effective use in most gas oils, amounts as low as 0.3% by weight have been found to be satisfactory. On the other hand the upper limits of additive concentration are determined by the solubility of the pour depressant material in the stocks used.

While in the foregoing there are described the preferred embodiments of the invention which have been found in practice to give satisfactory and reliable results, it is to be understood that the same is susceptible of modification in various particulars without departing from the spirit or scope of the invention or sacrificing any of its advantages.

*Table*

| Crude Oil Source | "Waxy" | Kuwait | Arabian | Ventura | Ventura | Ventura |
|---|---|---|---|---|---|---|
| Wax Content of Gas Oil Fraction, Wt. Percent | 2.8 | 2.9 | 4.3 | 5.5 | 5.5 | 5.5 |
| Pour Point, ° F | +40 | +25 | +25 | +50 | +50 | +50 |
| Pour Depressant | A[1] | A[1] | A[1] | A[1] | B[2] | C[3] |
| Concentration, Wt. Percent | 1.0 | 1.0 | 1.0 | 0.3 | 1.0 | 1.0 |
| Pour Point of Blend, ° F | −10 | 0 | −5 | −10 | +50 | +50 |
| Pour Point Depression, ° F | 50 | 25 | 30 | 60 | 0 | 0 |

A[1] represents the hydrogenated castor oil-urea reaction product of the invention.
B[2] represents a commercial product of the poly methacrylate type.
C[3] represents a second commercial product of the poly methacrylate type.

I claim:

1. A process for forming an oil-soluble reaction product suitable for use as an additive with which to lower below zero Fahrenheit the pour point of a waxy gas oil having a boiling range between 350° F. and 750° F. without the need for using subatmospheric pressures, which comprises contacting hydrogenated castor oil with a compound selected from the group consisting of urea and thiourea from about one-half to three hours at a temperature of from about 350° F. to about 600° F., said compound being added in a ratio from 0.3 mol to 15 mols per two mols of the hydrogenated castor oil, whereby a reaction product is formed as the upper layer in a reaction mixture, and separating said reaction product from said mixture.

2. A process as in claim 1 wherein the hydrogenated castor oil is reacted with urea for about one hour at about 500° F.

3. The process of claim 1 in which the castor oil and the said compound are heated together, and the approximate time of reaction and temperature is about an hour at 500° F.

4. The process of claim 1 in which the castor oil is first heated to about 500° F., the compound is urea, the urea is added while maintaining the temperature above 450° F., the mixture is then heated at about 500° F. for

about an hour, and the said mol ratio of urea to castor oil is 3:2.

5. The process of claim 1 in which the hydrogenated castor oil is glyceryl-12-hydroxy-stearate, the stearate is first heated to a temperature between 350° F. and 600° F. and the compound is then added so as to bring the mixture to the minimum temperature stated in the shortest possible time in order to minimize the formation of unwanted components.

6. As a new composition of matter suitable for use as a pour point depressant in waxy hydrocarbon gas oils, the oil-soluble reaction product prepared by the process of claim 1.

7. A mineral oil composition comprising a waxy gas oil having a boiling range between 350° and 750° F. in major amount based on the weight of the composition



and in excess of .3% by weight, sufficient to depress the pour point of said composition to below zero F., of the oil-soluble reaction product prepared by the process of claim 1.

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